

characterized by a pronounced maximum and falls off quite strongly on both sides; e.g. for dK (Pluth & Smith, 1979) the maximum is at $\varphi = 21^\circ$ and the descent of the curve is of the order of $1\%/1^\circ\Delta\varphi$; i.e. the aperture of the $8R$ of this zeolite ($\varphi = 9.6^\circ$) is reduced by $\sim 10\%$, compared with the maximal value, merely because of the effects of the tilt.

A program which models the zeolite A framework is available (Berset & Depmeier, 1984).

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References

- BERSET, G. & DEPMEIER, W. (1984). *ZEOLIT*. A Fortran program for modelling the zeolite A framework. Available on request.
- BRECK, D. W. (1974). *Zeolite Molecular Sieves*. New York: John Wiley.
- DEPMEIER, W. (1984). *Acta Cryst.* **B40**, 185-191.
- FYFE, C. A., KENNEDY, G. J., DE SCHUTTER, C. T. & KOKOTAILO, G. T. (1984). *J. Chem. Soc. Chem. Commun.* pp. 541-542.
- GIBBS, G. V., MEAGHER, E. P., NEWTON, M. D. & SWANSON, D. K. (1981). *Structure and Bonding in Crystals*, Vol. I, edited by M. O'KEEFFE & A. NAVROTSKY, pp. 195-225. New York: Academic Press.
- HAZEN, R. M. (1983). *Science*, **219**, 1065-1067.
- JIRÁK, Z., BOSACEK, V., VRATISLAV, S., HERDEN, H., SCHÖLLNER, R., MORTIER, W. J., GELLENS, L. & UYTTERHOEVEN, J. B. (1983). *Zeolites*, **3**, 255-258.
- KIM, Y., SUBRAMANIAN, V., FIROR, R. L. & SEFF, K. (1980). *Am. Chem. Soc. Symp. Ser.* No. 135, pp. 137-153.
- PAULING, L. (1930). *Z. Kristallogr.* **74**, 213-225.
- PLUTH, J. J. & SMITH, J. V. (1979). *J. Phys. Chem.* **83**, 741-749.
- PLUTH, J. J. & SMITH, J. V. (1983a). *J. Am. Chem. Soc.* **105**, 1192-1195.
- PLUTH, J. J. & SMITH, J. V. (1983b). *J. Am. Chem. Soc.* **105**, 2621-2624.
- SEFF, K. (1984). Private communication.
- SEFF, K. & MELLUM, M. D. (1984). *J. Phys. Chem.* **88**, 3560-3563.
- SMITH, J. V. (1984). Private communication.

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Electron Microscopy of Defects and Disorder in $\text{BaGa}_{12}\text{O}_{19}$

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Abstract

$\text{BaGa}_{12}\text{O}_{19}$ has been examined by high-resolution electron microscopy. It has a disordered structure based on a supercell of the magnetoplumbite structure. Disorder consists of the occurrence of different choices of origin of the supercell both within and between (0001) layers. Antiphase boundaries and more complex structures caused by interaction of the various types of defect are also found. It is suggested that the superstructure arises from a modification of the spinel blocks. Chemical microanalysis yields the atomic ratio $\text{Ga}/\text{Ba} = 11.7 \pm 0.8$.

Introduction

Adelsköld (1938) first determined the structure of magnetoplumbite, $\text{BaFe}_{12}\text{O}_{19}$, and a large number of compounds have since been reported to be isostructural (Morgan & Cirlin, 1982). Adelsköld found the symmetry to be $P6_3/mmc$, but subsequent investigators have found evidence for lower symmetry in some cases. Thus Verstegen (1973) observed some

reflections $000l$ with l odd in the powder pattern of $\text{BaGa}_{12}\text{O}_{19}$, a compound which is the subject of the present study. It is now well established that ' $\text{BaAl}_{11}\text{O}_{19}$ ' is in fact two distinct phases (I and II) with compositions different from the ideal one. These have recently been the subject of several electron microscope investigations (Morgan & Shaw, 1983; Iyi, Takekawa, Bando & Kimura, 1983; Yamamoto & O'Keeffe, 1984). Yamamoto & O'Keeffe showed from convergent-beam electron diffraction that phase I indeed had symmetry $P6_3/mmc$ but that phase II had trigonal or lower symmetry. All the electron microscope studies of phase II also found imperfect ordering corresponding to formation of supercell $\sqrt{3}a \times \sqrt{3}a \times c$. Recently Ganapathi, Gopalakrishnan & Rao (1984) reported the evidence of the existence of phase II crystals of $\text{BaFe}_{12}\text{O}_{19}$, and Bovin (1981) has also observed phase II behavior in plumboferrite, ' PbFe_4O_7 '. To date there is no satisfactory explanation for the occurrence of a superstructure or indeed even for the composition of the crystals.

In the magnetoplumbite structure there are layers with composition ABO_3 (here A is a large atom such

as Ba and B is a smaller one such as Ga) on the mirror planes. These are separated by slabs with composition $B_{11}O_{16}$ that have a local structure similar to that of spinel. For convenience we talk of 'mirror planes' in related structures even though mirror symmetry, *sensu stricto*, is absent. In the same spirit we talk of 'spinel slabs' although the evidence is strong that their structure is no longer that of spinel.

As part of a systematic investigation of these compounds, we have undertaken an investigation of $BaGa_{11}O_{19}$ to compare its behavior with that of the aluminate. According to Kovba, Lykova, Kobzareva, Lopato & Shevchenko (1975), this phase occurs as a stoichiometric phase stable below 1803 K in the BaO-Ga₂O₃ system. We find that this material also has a

complex superstructure and is rich in defects and disorder.

Experimental

$BaGa_{12}O_{19}$ and $BaGa_2O_4$ (for use as an analytical standard) were prepared by heating stoichiometric mixtures of $BaCO_3$ and Ga_2O_3 in air. The hexagallates were annealed at 1773 K for 3 d. The identity of the phases obtained was confirmed from Guinier X-ray patterns.

Samples for electron microscopy were prepared by scooping crushed particles floating in an acetone suspension onto a copper grid covered with a holey-carbon film and examined in a JEM 200CX electron

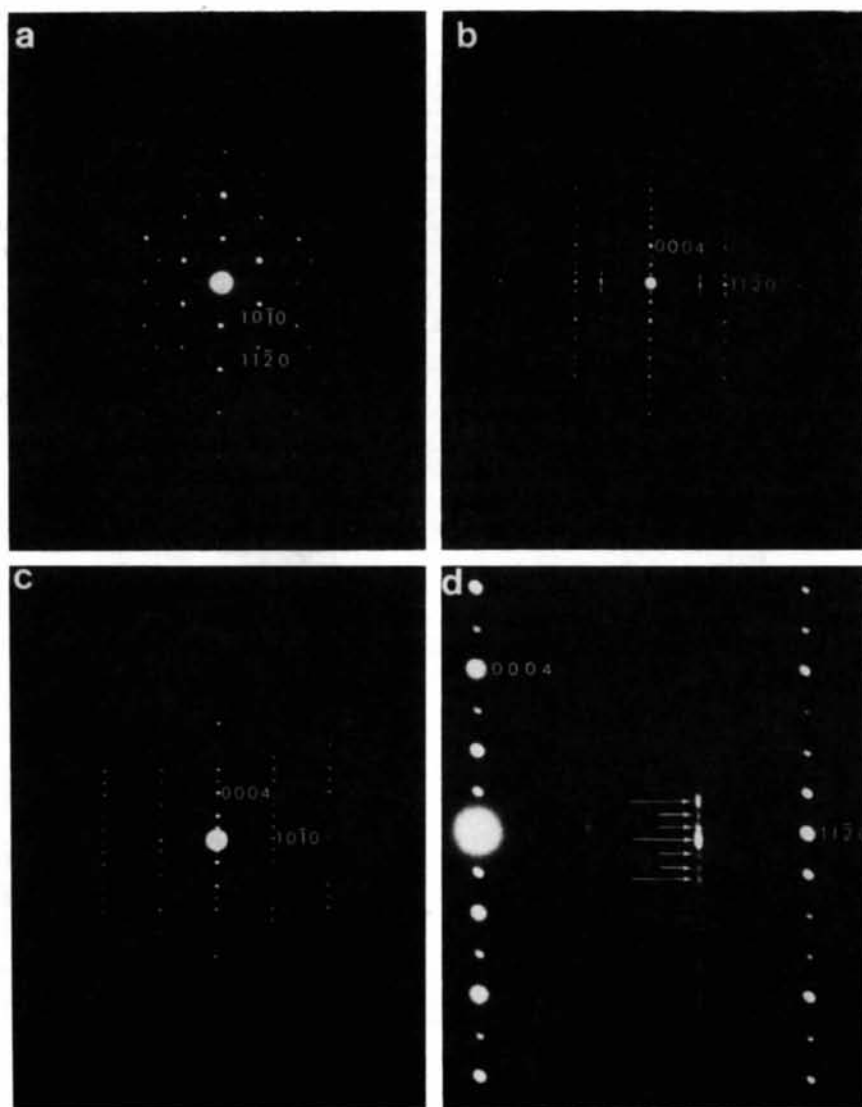


Fig. 1. Diffraction patterns from a $BaGa_{12}O_{19}$ crystal: (a) [0001], (b) $[1\bar{1}00]$, (c) $[11\bar{2}0]$; (d) is an enlargement of part of (b) showing superstructure spots with $l = \pm \frac{1}{3}$ and $\pm \frac{2}{3}$ (arrowed). Indices refer to the magnetoplumbite subcell.

microscope. Chemical microanalyses were performed in a Philips 400T microscope equipped with a Kevex energy-dispersive spectrometer. A Tracor Northern 2000 multichannel analyzer system was used to integrate the peak intensities in the X-ray spectrum after background subtraction.

Diffraction patterns

All the crystals examined had diffraction patterns that closely resembled those of phase II ' $\text{BaAl}_{11}\text{O}_{19}$ ' (Yamamoto & O'Keeffe, 1984). Diffraction patterns are shown for the $[0001]$, $[1\bar{1}00]$ and $[11\bar{2}0]$ zones in Fig. 1 indexed according to the magnetoplumbite cell ($a = 5.850$, $c = 23.77$ Å)—note that throughout the paper these indices are used. The $[0001]$ zone pattern clearly shows superlattice spots at $(n/3)\{hh\bar{2}h0\}$ corresponding to a $\sqrt{3}a \times \sqrt{3}a$ supercell. The corresponding $[1\bar{1}00]$ patterns showed that there is considerable streaking along $[0001]$. These rods of intensity at $\{n/3\ n/3\ \bar{2}n/3\ l\}$ do, however, show peaks at $l = m/3$ indicating ordering along the c axis also as shown in Fig. 1. As Yamamoto & O'Keeffe (1984) have discussed, the disorder can be interpreted as arising from a disordered choice of the origin from one of three possibilities (A, B or C) in a given (0001) plane as illustrated in Fig. 2; the figure also illustrates why the disorder is visible in $\langle 1\bar{1}00 \rangle$ but not in $\langle 11\bar{2}0 \rangle$ zones. The superstructure spots alluded to above arise from the occurrence of ordered sequences ...ABC...; these can be observed in regions of the images.

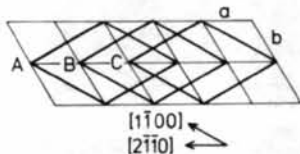


Fig. 2. The relationship of the supercell to the magnetoplumbite cell showing possible choices of origin. Note that indices refer to the magnetoplumbite cell.

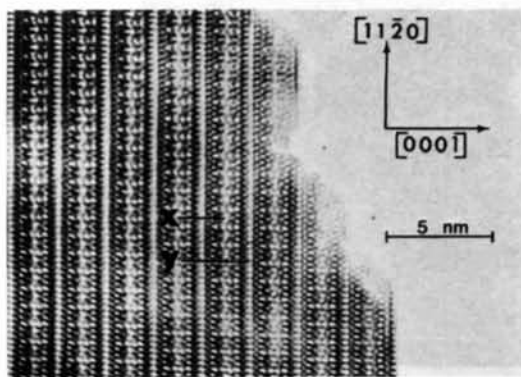


Fig. 3. Part of an image corresponding to the diffraction pattern in Fig. 1(b). X and Y refer to the two types of mirror plane.

Although it was chosen for illustration as it shows evidence of superstructure ordering at $(n/3\ n/3\ -2n/3\ m/3)$, it might be noted that the diffraction pattern shown in Fig. 1(b) and (d) is somewhat atypical in that the $(\frac{2}{3}\ \frac{2}{3}\ -\frac{4}{3}\ l)$ intensity is greater than that at $(\frac{1}{3}\ \frac{1}{3}\ -\frac{2}{3}\ l)$. In general the intensity in these rows is more nearly equal [compare Fig. 1(e) of Yamamoto & O'Keeffe (1984)]. We return to this point below.

High-resolution images

As for the aluminate phase II (Yamamoto & O'Keeffe, 1984), and as might be expected from the diffraction patterns, images with the beam parallel to $[1\bar{1}00]$ are the most informative and thus will be the only ones discussed here. Fig. 3 shows part of an image of the crystal that gave the diffraction pattern of Fig. 1(b). Notable is the fact that the periodicity along $[0001]$ is c indicating the loss of the magnetoplumbite 6_3 axis (which would have given a periodicity of $c/2$). The mirror planes (on which the Ba atoms would lie in the ideal magnetoplumbite structure) remain in a local sense, but, as alternate ones have very different contrast, presumably they correspond to regions of different local structure. For future reference we label them X and Y planes.

Also very clear (especially when the images are viewed along $[0001]$ and at a glancing angle to the page) is the disorder in the stacking of the layers along $[0001]$ corresponding to different choices A, B

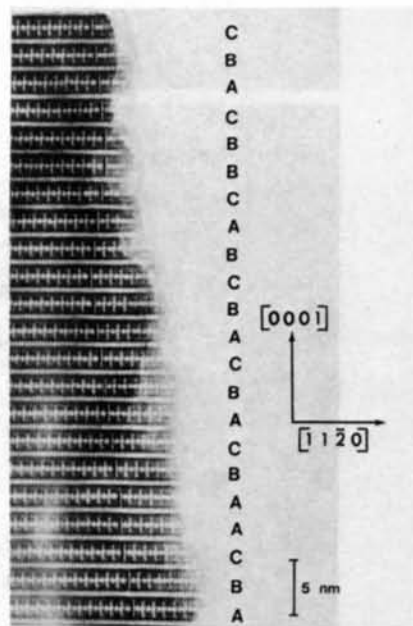


Fig. 4. A $[1\bar{1}00]$ image showing disorder of the origin of the supercell in successive layers along the c axis. The lower part of the figure shows a region ordered ...ABC...

or *C* of the origin of the supercell as shown in Fig. 4. Note the occurrence of an ordered sequence ...*ABC*... in the lower part of the figure. Sequences ...*AAA*... are also fairly common (visible in areas of Figs. 3 and 5), but sequences ...*AB*... are much rarer. When the sequence is *ABC* one can see the beginning of a development of periodicity of $(\frac{2}{3})d_{11\bar{2}0}$ along $[11\bar{2}0]$ (this is particularly evident in the lower right corner of the micrograph in Fig. 6 which may be compared with the lower right of Fig. 3). The corresponding diffraction patterns have the intensity in $\{\frac{1}{3}\frac{1}{3}-\frac{2}{3}l\}$ reduced relative to that in $\{\frac{2}{3}\frac{2}{3}-\frac{4}{3}l\}$. It is possible, therefore, that the slabs that stack *ABC* have a different structure than those that stack *AA*.

Another common feature of the crystals investigated was the occurrence of antiphase boundaries such as shown in Fig. 5. These are usually jagged

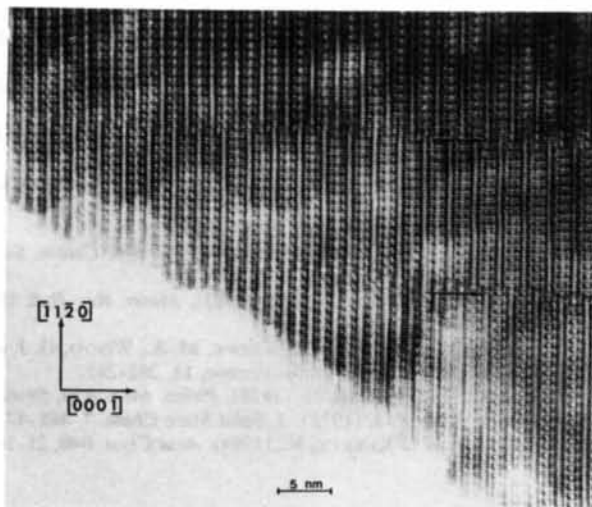


Fig. 5. An image of antiphase boundaries (arrowed).

boundaries, approximately normal to $[11\bar{2}0]$, across which the sequence of 'mirror' planes changes from ...*XY*... to ...*YX*... An important point of these observations is that they demonstrate that the different contrast from the *X* and *Y* planes is not an artifact of beam tilt, which is known to produce spurious contrast and loss of symmetry even for small tilt angles (Smith, Saxton, O'Keefe, Wood & Stobbs, 1983). Notable is the fact that we have never observed defects *XX* or *YY* etc.

An even more complex defect is shown in Fig. 6. As the crystal is rather thick, and thus the image less easy to interpret, we have sketched the prominent features on the right of the figure. The main feature is a 'Z' formed by the trace of $(11\bar{2}1)$ and $(11\bar{2}\bar{1})$ planes. It is tempting to associate this feature with a faulted *Z* dislocation dipole such as has been observed in silicon by Spence & Kolar (1979). Reference to Fig. 6 shows that a new type of defect is appearing; this is disorder in the choice of origin of the supercell in a given layer. In the sketch this appears as variations in the spacing in the horizontal lines in an *X* layer. Normally these are spaced $3d_{11\bar{2}0}$ apart but, in the region of the *Z*, spacings of $2d_{11\bar{2}0}$ and $4d_{11\bar{2}0}$ can be seen (for example at the places marked *P* and *Q* in the figure). Fig. 6 thus represents a complex ordering due to the interaction of three types of defect: disorder of choice of origin in successive (0001) layers, similar disorder in a single layer, and antiphase boundaries.

Chemical analyses

The normalized standard deviation in the measured $I_{\text{Ba}}/I_{\text{Ga}}$ ratios for twelve crystals was the same as that for the same ratios obtained from twelve crystals of BaGa_2O_4 (which is assumed to be stoichiometric). Accordingly the results were averaged and the ratio method (Cliff & Lorimer, 1972) gave the chemical

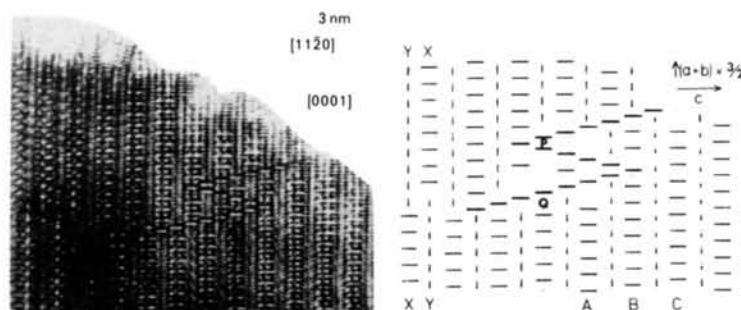


Fig. 6. Left: image of an extended *Z* defect. One arm of the *Z* terminates at the edge of the crystal. The other arm ends at a ragged antiphase boundary. Right: a schematic interpretation of the image. The fine lines are a grid with dimensions of the projected supercell as a guide to the eye. *X* and *Y* refer to the two types of mirror plane and *A*, *B* and *C* refer to three *X* planes with different origins of the supercell. The bold horizontal lines represent the regions of lightest contrast in the region of the *X* planes. (This light contrast can be seen more clearly in Fig. 3 where it appears as a row of four white dots.)

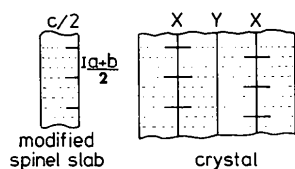


Fig. 7. Schematic representation of a spinel slab modified in the region of the horizontal bars and of how these slabs are put together in the crystal.

analysis $\text{Ga}/\text{Ba} = 11.7 \pm 0.8$ (95% confidence limits), so that, in contrast to the aluminate, the gallate is close to (if not at) the stoichiometric composition.

Discussion

It is clear from the results that $\text{BaGa}_{12}\text{O}_{19}$ does not have the magnetoplumbite structure although, from the magnitude of the lattice parameters of the subcell, it must have a closely related one. The occurrence of a $\sqrt{3}a \times \sqrt{3}a \times c$ supercell and the appearance of the lattice images suggests that the structure is similar to that of the phase II aluminate. However, our samples appear to be close to the ideal composition so it is unlikely that the supercell arises from ordering of empty sites or excess cations in the mirror planes. In fact, examination of images such as that shown in Fig. 3 indicates that it is probably the 'spinel' slabs that are modified as well as, perhaps, the arrangement on the mirror planes. In Fig. 7 we show schematically a crystal built up of modified spinel slabs. Also in that figure is suggested the reason that X and Y planes always alternate—for structural reasons, the 'mirror' planes must indeed be true local mirrors.

It is also clear that these materials will resist the classical diffraction methods of structure analysis. However, if adequate trial structures can be generated, image calculations should be able to eliminate incorrect models. This task is now being undertaken. The results presented here help in providing restraints on the models.

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References

- ADELSKÖLD, V. (1938). *Ark. Kemi Mineral. Geol.* **12A**, 1-9.
 BOVIN, J.-O. (1981). *Geol. Foeren. Stockholm Foerh.* **103**, 122-124.
 CLIFF, C. & LORIMER, G. W. (1972). *Proceedings of the Fifth European Congress on Electron Microscopy*, p. 140. Bristol: Institute of Physics.
 GANAPATHI, L., GOPALAKRISHNAN, J. & RAO, C. N. R. (1984). *Mater. Res. Bull.* **19**, 669-672.
 IYI, N., TAKEKAWA, S., BANDO, Y. & KIMURA, S. (1983). *J. Solid State Chem.* **47**, 34-40.
 KOVBA, L. M., LYKOVA, L. N., KOBZAREVA, V. P., LOPATO, L. M. & SHEVCHENKO, A. V. (1975). *Zh. Neorg. Khim.* **20**, 1970-1973; *Russ. J. Inorg. Chem.* **20**, 1098-1100.
 MORGAN, P. E. D. & CIRLIN, E. H. (1982). *J. Am. Ceram. Soc.* **65**, C114-C115.
 MORGAN, P. E. D. & SHAW, J. M. (1983). *Mater. Res. Bull.* **18**, 539-542.
 SMITH, D. J., SAXTON, W. O., O'KEEFE, M. A., WOOD, G. J. & STOBBS, W. M. (1983). *Ultramicroscopy*, **11**, 262-282.
 SPENCE, J. C. H. & KOLAR, H. (1979). *Philos. Mag.* **A39**, 59-63.
 VERSTEGEN, J. M. P. J. (1973). *J. Solid State Chem.* **7**, 468-473.
 YAMAMOTO, N. & O'KEEFE, M. (1984). *Acta Cryst.* **B40**, 21-26.